

## METHOD FOR FORMING THIN FILM

## METHOD FOR FORMING THIN FILM

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EC Classification:  
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### Abstract

**PROBLEM TO BE SOLVED:** To relax stress generated in a thin film, and improve adhesion to the thin film, and further raise the film developing rate on a substrate by the Atomic Layer Epitaxy(ALE) method.

**SOLUTION:** In forming Al<sub>2</sub>O<sub>3</sub> film by ALE method using TMA and H<sub>2</sub>O on a glass substrate, CH<sub>3</sub>OH evaporated before forming film or during formation of film is introduced and surface treatment for increasing surface hydroxyl group concentration of the ground surface is carried out by exposing the ground surface in gas atmosphere of CH<sub>3</sub>OH.

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**Bibliography.**

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Summary.

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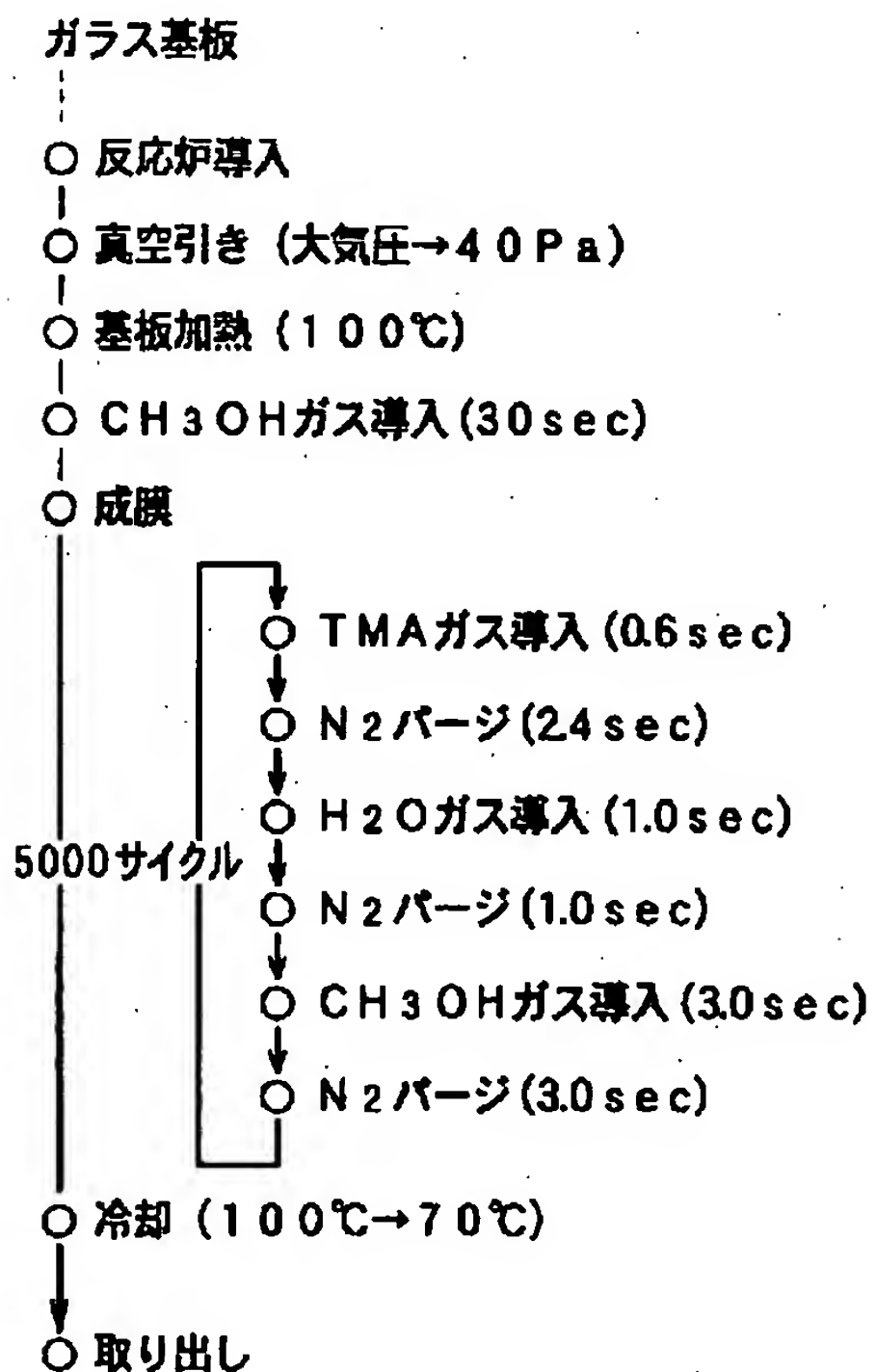
(57) [Abstract]

[Technical problem] In the formation method of the thin film which forms a thin film by the ALE method on a substrate, while easing the stress generated in a thin film, the adhesion to the ground of a thin film is raised and a membrane formation rate is raised further.

[Means for Solution] Surface treatment which raises the surface-water-of-aggregate acid-radical concentration of a ground side is performed by introducing CH<sub>3</sub>OH evaporated before membrane formation and during membrane formation, and exposing a ground side into the gas atmosphere of a CH<sub>3</sub>OH molecule in forming 2Oaluminum<sub>3</sub> film by the ALE method which used TMA and H<sub>2</sub>O on the glass substrate.

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CLAIMS

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[Claim(s)]

[Claim 1] The formation method of the thin film characterized by being the method of forming a thin film by the atomic-layer grown method on a substrate, and performing surface treatment which raises surface-water-of-aggregate acid-radical concentration to a ground side at one [ at least ] time under membrane formation of the aforementioned thin film, and before membrane formation.

[Claim 2] For the raw material of the aforementioned thin film, the aforementioned surface treatment is the formation method of the thin film according to claim 1 characterized by carrying out using a different material.

[Claim 3] The aforementioned surface treatment is the formation method of the thin film according to claim 1 or 2 characterized by being made by exposing the aforementioned ground side into the gas atmosphere of a molecule with a hydroxyl group.

[Claim 4] The gas of a molecule with the aforementioned hydroxyl group is the formation method of the thin film according to claim 3 characterized by considering as the state where the molecule concerned was made to plasma-ize.

[Claim 5] The aforementioned surface treatment is the formation method of the thin film according to claim 1 or 2 characterized by being made by spraying the

liquid of the molecule which has a hydroxyl group to the aforementioned ground side before membrane formation of the aforementioned thin film.

[Claim 6] The claim 3 to which a molecule with the aforementioned hydroxyl group is characterized by combining H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, alcohols, or these two sorts or more, or the formation method of the thin film any one publication of five.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the formation method of the thin film which forms a thin film by the atomic-layer grown method (Atomic Layer Epitaxy) on a substrate.

[0002]

[Description of the Prior Art] An atomic-layer grown method (it is called the ALE method Atomic Layer Epitaxy and the following) is one atomic layer or a method which carries out a crystal growth at a time one molecular layer by supplying two or more sorts of raw materials (an element or compound) by turns, and using the difference of the adsorption reaction on the front face of a substrate, and the vapor pressure of a raw material and the purpose product.

[0003]

[Problem(s) to be Solved by the Invention] In the ALE method, the adsorption mechanism of a material gas molecule is restricted, when the autogenous-control type adsorption mechanism which can be expressed with a Langmuir type is dominant. By the Langmuir type adsorption mechanism, in the surface coverage of a raw material, when  $\theta_{\text{tai}}$  and a rate-of-adsorption constant are set to  $K_a$  and a desorption rate constant is set to  $K_d$  under the partial pressure  $P_i$  of a raw material, a rate of adsorption is expressed with  $K_a P_i (1 - \theta_{\text{tai}})$ , and a desorption rate is expressed with  $K_d \theta_{\text{tai}}$ . Here, since a rate of adsorption and a desorption rate are equal, when  $K = (K_a / K_d)$ , surface coverage  $\theta_{\text{tai}}$  of a raw material is shown by the following formula 1.

[0004]

[Equation 1]  $\theta_{\text{tai}} = K_a P_i / (K_d + K_a P_i) = K P_i / (1 + K P_i)$

Here, if  $K P_i$  is larger than 1 enough, namely, the amount of the atom which exists in a gaseous phase, or a molecule is in the supersaturation state to the amount of adsorption, a monoatomic layer or monomolecular-layer formation will be attained.

[0005] However, in  $K P_i$ , in almost all cases, the steric hindrance and the adsorption site of adsorption are uneven, and a monoatomic layer or monomolecular-layer formation is not realized [ in / a ground side / as a sufficiently larger state than 1 ]. For example, by the reaction of  $\text{AlCl}_3$  and  $\text{H}_2\text{O}$ , if a layer is grown up by the ALE method at about 500 degrees C, it will become the membrane formation rate of 0.045nm/a cycle, and a part for one molecular layer will not be filled with this.

[0006] Although possibility of being because  $K P_i$  not being locally larger than 1 enough is also considered by things, a gas flow, etc. with low response probability, this is considered that it is the cause of main that decline in surface coverage is large so that it may state below. First, in an ALE growth process, the element which is sticking to a ground side, or a compound reacts with the element and compound which stick to a degree.



[0007] At this time, the element which sticks to a degree, and a compound react with two or more elements and compounds to which it has already stuck depending on a system. That is, since the bonding strength (intermolecular force and Van der Waals force) of the generated purpose product works also to the element or compound which stuck to the approaching adsorption site in order that one element and compound which stick to a degree may react to two or more adsorption sites with the element and compound to which it has already stuck and may combine with them, a microscopic distortion arises.

[0008] And since combination which is sticking to a ground side is a strong combination of hydrogen bond etc. when physical adsorption to which it sticks in gravity, an electrostatic force, etc. is removed, the above-mentioned distortion will become very large. If this continues membrane formation by the ALE method owing to, as a result, a film contracts in the done thin film, and if like is supposed and it says, it will be thought that a tensile stress occurs.

[0009] Here, when bonding strength reaches among such two or more adsorption sites, even if it is the case where adsorption is uniformly made by all adsorption sites even if, a microscopic distortion arises somewhat in a thin film for the reason for the above. Although it reacts similarly too especially when adsorption to a ground side is uneven, minute hole (hole produced by the portion in which it is the adsorption site to which an element etc. should stick, and adsorption is not made) exists in this case.

[0010] The bonding strength which commits this minute hole to a contiguity element or a compound since it is usually larger than the interatomic distance of the purpose product after a reaction becomes larger. Therefore, when adsorption is uneven, the above-mentioned microscopic distortion also becomes large and poses a problem. Moreover, it is distinct that the adhesion of a thin film falls that adsorption to a ground side is uneven. Furthermore, in a membrane formation field, a portion with a late membrane formation rate arises partially that adsorption is uneven in a bird clapper, and the whole membrane formation rate becomes late as a result.

[0011] As mentioned above, although the ALE method can obtain a thin film with the outstanding surface coverage from the growth mechanism according to this invention person's etc. examination, a tensile stress essentially occurs in a thin film, and the crack of a thin film and the problem of ablation arise from the imperfection of adsorption to the ground side of the element or a compound, and the problem that a fall and membrane formation rate of the adhesion of a thin film are late is also produced.

[0012] this invention raises the adhesion to the ground of a thin film while easing the stress generated in a thin film in view of the above-mentioned problem in the formation method of the thin film which forms a thin film by the ALE method on a substrate, and it aims at raising a membrane formation rate further.

[0013]

[Means for Solving the Problem] this invention is made based on the idea whether processing which raises the surface density of the adsorption site of gas to a ground side during membrane formation should be performed, before forming membranes by the ALE method.

[0014] It is the hydroxyl group on a ground side which determines an adsorption site. Since a hydroxyl group generates the big bonding strength by hydrogen bond, this is because it can be made easy to draw the element and compound approaching a ground and to adsorb. That is, by performing hydroxyl-group-ized termination processing in which a ground side is made to hydroxyl-group-ize, the surface density of an adsorption site can be improved and adsorption of the material gas of a thin film can be promoted.

[0015] For example, when a ground side is  $\text{TiO}_2$ , the process which a surface-water-of-aggregate acid radical produces in a ground side is considered like drawing 5 by making this ground side expose to the gas of  $\text{H}_2\text{O}$ . coordination --  $\text{H}_2\text{O}$  which stuck to unsaturated surface  $\text{Ti}^{4+}$  ion carries out adjoining  $\text{O}^{2-}$  and hydrogen bond, and two surface-water-of-aggregate acid radicals are further generated by cutting of OH combination of adsorption  $\text{H}_2\text{O}$  It is thought that a surface-water-of-aggregate acid radical generates by the chemical absorption of

H<sub>2</sub>O by the almost same mechanism about other oxides.

[0016] As a result of performing experiment examination based on such an idea, invention according to claim 1 to 6 is a method which is found out and forms a thin film by the atomic-layer grown method on a substrate, and is characterized by performing surface treatment which raises surface-water-of-aggregate acid-radical concentration to a ground side at one [ at least ] stage under membrane formation of a thin film, and before membrane formation.

[0017] Since according to it the surface density of the adsorption site in a ground side can be improved and adsorption of thin film material gas can be promoted, the adsorption of an element and a compound to a ground side equalizes more. Therefore, while easing the stress generated in a thin film, the adhesion to the ground of a thin film can be raised and a membrane formation rate can be raised further.

[0018] Moreover, in invention of a claim 2, the above-mentioned surface treatment is characterized by carrying out using a different material from the raw material of a thin film. This surface treatment can be prevented from participating the surface treatment concerned in a thin film formation reaction more suitably, if material which is different from the introductory stage of a thin film raw material with a thin film raw material like this invention although carried out by shifting timing is used so that it may not participate in the reaction for thin film formation directly.

[0019] The here above-mentioned surface treatment can be performed by exposing a ground side into the gas atmosphere of a molecule with a hydroxyl group (invention of a claim 3). In this case, the thing (invention of a claim 4) which made the gas of a molecule with a hydroxyl group the state where the molecule concerned was made to plasma-ize, then the above-mentioned surface treatment can be performed more efficiently. Moreover, the above-mentioned surface treatment can also be performed by spraying the liquid of the molecule which has a hydroxyl group to a ground side before membrane formation of a thin film (invention of a claim 5).

[0020] Moreover, as a molecule with the hydroxyl group used for these surface treatment methods, what combined  $H_2O$ ,  $H_2O_2$ , alcohols, or these two sorts or more is employable.

[0021] In addition, the sign in the parenthesis of each above-mentioned means is an example which shows a correspondence relation with the concrete means of a publication to the operation gestalt mentioned later.

[0022]

[Embodiments of the Invention] The method of forming a thin film by the atomic-layer grown method (the ALE method) on a substrate installs a substrate in a reactor, and is made by introducing the material gas of a thin film into a reactor. In here, even if it performs execution of the surface treatment (only henceforth surface treatment) which raises surface-water-of-aggregate acid-radical concentration to a ground side with the stage of both under membrane formation of a thin film, and before membrane formation and goes only during membrane formation, you may go only before membrane formation.

[0023] The compound which consists of a molecule with a hydroxyl group as a material used for this surface treatment can be used, and, specifically, what combined  $H_2O$ ,  $H_2O_2$ , alcohols, or these two sorts or more can be adopted. And as the method of the surface treatment using the charge of these surface treatment material, the following methods are employable.

[0024] First, the compound which consists of a molecule with a hydroxyl group beforehand is evaporated, and the method of exposing a ground side to this gas (gas of molecule with hydroxyl group) atmosphere is mentioned. For example, what is necessary is for heating etc. to make it evaporate by carrying out the raw material bottle containing the compound with hydroxyl groups, such as a methanol and water, and just to introduce into the reactor in which the substrate is contained by carrier gas, such as  $N_2$  and Ar. It is exposed by that cause into the gas atmosphere of the molecule in which the ground side of the thin film in a substrate has a hydroxyl group, and the above-mentioned surface treatment is performed to a ground side.

[0025] Here, the thing which made the gas of a molecule with a hydroxyl group the state where the molecule concerned was made to plasma-ize, then the above-mentioned surface treatment can be performed more efficiently. namely, the inside of a reactor -- setting -- countering -- alienation -- the electrode of the arranged couple is prepared, and where it installed the substrate and high-frequency voltage is impressed among these electrodes, the gas of a molecule with a hydroxyl group is introduced Then, since the molecule concerned is plasma-ized (for example, OH- and OH radical arise in CH<sub>3</sub>OH), a activity reaction becomes possible on a substrate and the efficient surface treatment of it becomes possible.

[0026] Moreover, you may make it spray the liquid of the compound which consists of a molecule with a hydroxyl group to a ground side. For example, it is possible to spray into the reactor by which the substrate has been arranged using an injector etc. However, there are very many compounds which physisorb the ground side described above in this case compared with the method of exposing to the gas atmosphere of a molecule with a hydroxyl group, and this checks the layer growth by the ALE method.

[0027] Therefore, it is desirable to heat a substrate a little, or to make it atmosphere, such as N<sub>2</sub> and Ar gas, and to remove a part for this physical adsorption. Furthermore, if optimum dose spraying of the liquid of the compound which has a hydroxyl group in the reactor made into the vacuum is carried out, in order to evaporate by rapid adiabatic expansion, the surface treatment by spraying becomes more efficiently possible.

[0028] Next, while an example is shown about this operation gestalt, it explains further. The case (example of comparison) where it does not carry out with the case where surface treatment by gas exposure of a methanol (CH<sub>3</sub>OH) is performed is shown by TMA (tetramethyl aluminum, AlCl<sub>3</sub>) and H<sub>2</sub>O on a glass substrate, carrying out ALE growth of the 2Oaluminum<sub>3</sub> film as a thin film.

[0029] First, in the formation method of the thin film which forms 2Oaluminum<sub>3</sub> film on a glass substrate by the ALE method which used TMA and H<sub>2</sub>O, the case

(example of this operation gestalt) where surface treatment by CH<sub>3</sub>OH is performed before membrane formation of Al<sub>2</sub>O<sub>3</sub> film and during membrane formation is shown. The flow is shown in drawing 1 .

[0030] 40mmx40mm and the glass substrate with a thickness of 1.1mm were put into the reactor. The reactor was made into the about 40Pa vacuum, the substrate was heated for about 400 sccms of N<sub>2</sub> gas with the sink, and substrate temperature was stabilized at 100 degrees C. CH<sub>3</sub>OH was evaporated at 30 degrees C within the raw material bottle, and it introduced into the reactor for 30 seconds by N<sub>2</sub> gas 400sccm. This introduction of CH<sub>3</sub>OH performed surface treatment before membrane formation.

[0031] Then, it introduced into the reactor by N<sub>2</sub> gas 400sccm which is carrier gas in order of TMA, H<sub>2</sub>O, and CH<sub>3</sub>OH. TMA and H<sub>2</sub>O were evaporated at the room temperature within the raw material bottle, and were introduced into the reactor by N<sub>2</sub> gas 400sccm which is carrier gas.

[0032] The gas to a reactor introduced N<sub>2</sub> gas for 2.4 seconds as a purge, after introducing Evaporation TMA for 0.6 seconds first. Then, the N<sub>2</sub> purge was similarly formed for evaporation H<sub>2</sub>O in the gas installation time for 1.0 seconds for 1.0 seconds. Then, in order to perform surface treatment under membrane formation, evaporation CH<sub>3</sub>OH was introduced into the reactor for 3 seconds by N<sub>2</sub> gas 400sccm, and in order to exhaust CH<sub>3</sub>OH in a gaseous phase, the N<sub>2</sub> purge was performed 3 sccms.

[0033] This TMA introduction -> purge ->H<sub>2</sub>O introduction -> purge ->CH<sub>3</sub>OH introduction -> repeat membrane formation was performed for the cycle of a purge 5000 times. In the meantime, the pressure of a reactor is 150-320Pa, and substrate temperature was held at 100 degrees C at the heater in a reactor. After membrane formation was completed, when neglect cooling was performed and substrate temperature became 70 degrees C, carrying out 400sccm introduction of the N<sub>2</sub> gas, the reactor was made into atmospheric pressure, and the substrate was taken out.

[0034] By this technique, Al<sub>2</sub>O<sub>3</sub> film of about 480nm of thickness was



obtained. The membrane formation rate at this time was 0.096nm/a cycle. Moreover, the stress of  $\text{Al}_2\text{O}_3$  film measured from the amount of curvatures of the glass substrate before and behind membrane formation was a tensile stress, and was 220MPa.

[0035] Next, as an example of comparison, ALE growth of the  $\text{Al}_2\text{O}_3$  film is carried out by TMA and  $\text{H}_2\text{O}$  on a glass substrate, and the case where surface treatment is not performed is shown. The flow is shown in drawing 2. The same glass substrate of size as the above is put into a reactor, like the above-mentioned example, the reactor was made into the about 40Pa vacuum, the substrate was heated for about 400 sccms of  $\text{N}_2$  gas with the sink, and substrate temperature was stabilized at 100 degrees C.

[0036] Then, it introduced into the reactor by TMA and  $\text{N}_2$  gas 400sccm which is carrier gas in order of  $\text{H}_2\text{O}$ . First, the gas to a reactor introduced  $\text{N}_2$  gas for 2.4 seconds as a purge for removing superfluous TMA which exists in gaseous phases other than the molecule which stuck to the substrate front face, after introducing Evaporation TMA for 0.6 seconds. Then, 1.0sec(s) and the  $\text{N}_2$  purge were similarly formed for evaporation  $\text{H}_2\text{O}$  in the gas installation time for 4.0 seconds.

[0037] This TMA introduction -> purge ->  $\text{H}_2\text{O}$  introduction -> repeat membrane formation was performed for the cycle of a purge 5000 times. In the meantime, the pressure of a reactor is 150-300Pa, and substrate temperature was held at 100 degrees C at the heater in a reactor. After membrane formation was completed, when neglect cooling was performed and substrate temperature became 70 degrees C, carrying out 400sccm introduction of the  $\text{N}_2$  gas, the reactor was made into atmospheric pressure, and the substrate was taken out.

[0038] By this technique,  $\text{Al}_2\text{O}_3$  film of about 400nm of thickness was obtained. The membrane formation rate at this time was 0.08nm/a cycle. Moreover, the stress of  $\text{Al}_2\text{O}_3$  film measured from the amount of curvatures of the glass substrate before and behind membrane formation was a tensile stress, and was 430MPa.

[0039] Drawing 3 is drawing showing the effect of the stress relaxation of this invention concretely based on the result of the example of this above-mentioned operation gestalt, and the example of comparison. The direction which performed surface treatment is understood that stress is eased. Moreover, drawing 4 is drawing showing concretely the effect of the improvement in a membrane formation rate of this invention based on the result of the example of this above-mentioned operation gestalt, and the example of comparison. When surface treatment is performed, compared with the case where it does not carry out, a membrane formation rate increases quick about 1.2 times, and its membrane formation rate is also improving. Moreover, since the membrane formation rate improved, adsorption equalizes and it can be said that the adhesion of a thin film can also be improving.

[0040] Thus, in the ALE method, since the surface density of the adsorption site in a ground side can be improved and adsorption of thin film material gas can be promoted by performing surface treatment which raises surface-water-of-aggregate acid-radical concentration to a ground side at one [ at least ] stage under membrane formation of a thin film, and before membrane formation, the adsorption of an element and a compound to a ground side equalizes more. Therefore, while easing the stress generated in a thin film, the adhesion to the ground of a thin film can be raised and a membrane formation rate can be raised further.

[0041] Here, the above-mentioned surface treatment can realize suitably making it not participate in the reaction for thin film formation of surface treatment directly by [ from the raw material (the above-mentioned example TMA and H<sub>2</sub>O) of a thin film / different ] carrying out by using material (the above-mentioned example CH<sub>3</sub> OH). In addition, you may perform surface treatment with the same material as a thin film raw material. For example, in the case of the above-mentioned example, you may perform surface treatment by H<sub>2</sub>O. In this case, what is necessary is just made to perform the cycle of an H<sub>2</sub>O introduction -> purge as a charge of H<sub>2</sub>O introduction -> purge -> surface treatment material as a TMA



introduction -> purge -> thin film raw material.

[0042] Moreover, as a charge of surface treatment material, you may choose from the molecule with ether linkage, a carboxyl group, and a carbonyl group of for example, an ether system compound, a ketone system compound, a carboxylic-acid system compound, etc. suitably besides a molecule with a hydroxyl group.

[0043] In addition, this invention can be applied when forming the protective coat which covers and protects this structure in the organic EL element which comes to arrange the structure which comes to insert an organic luminous layer into inter-electrode [ of a couple ] for example, on a substrate.

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#### DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the flow chart showing the formation method of the thin film concerning the operation gestalt of this invention.

[Drawing 2] It is the flow chart showing the formation method of the thin film as an example of comparison.

[Drawing 3] It is drawing showing concretely the effect of the stress relaxation of the thin film of this invention.

[Drawing 4] It is drawing showing concretely the effect of the improvement in a membrane formation rate of this invention.

[Drawing 5] It is drawing showing the presumed mechanism of the process which the surface-water-of-aggregate acid radical by H<sub>2</sub>O exposure in case a ground side is TiO<sub>2</sub> produces.

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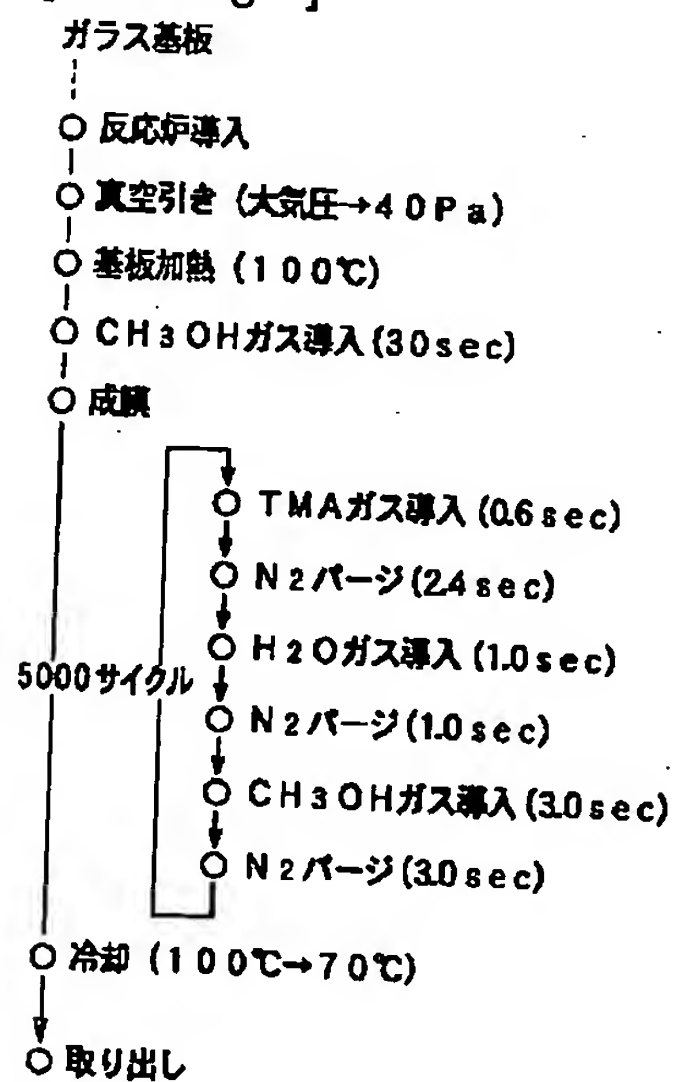
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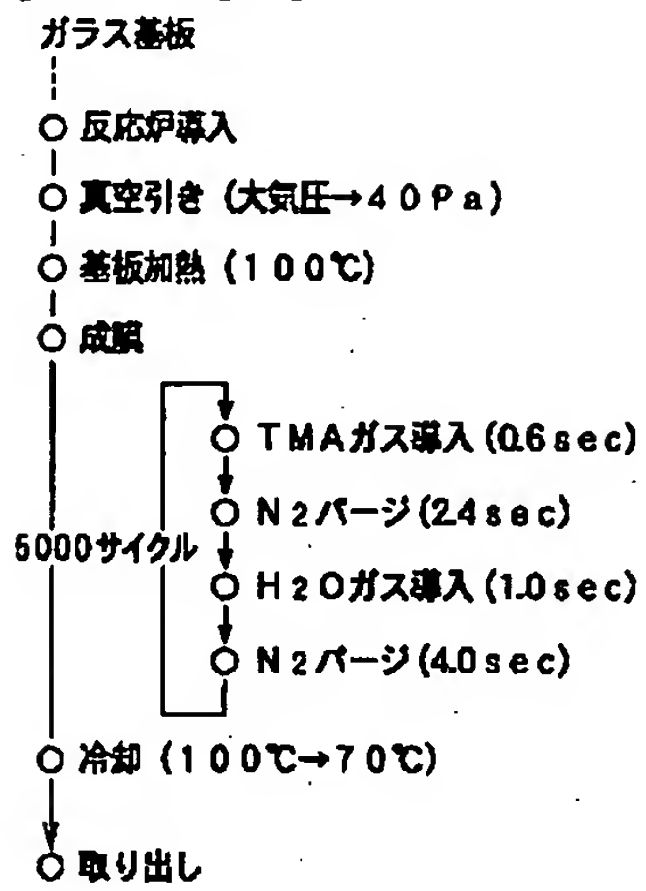
DRAWINGS

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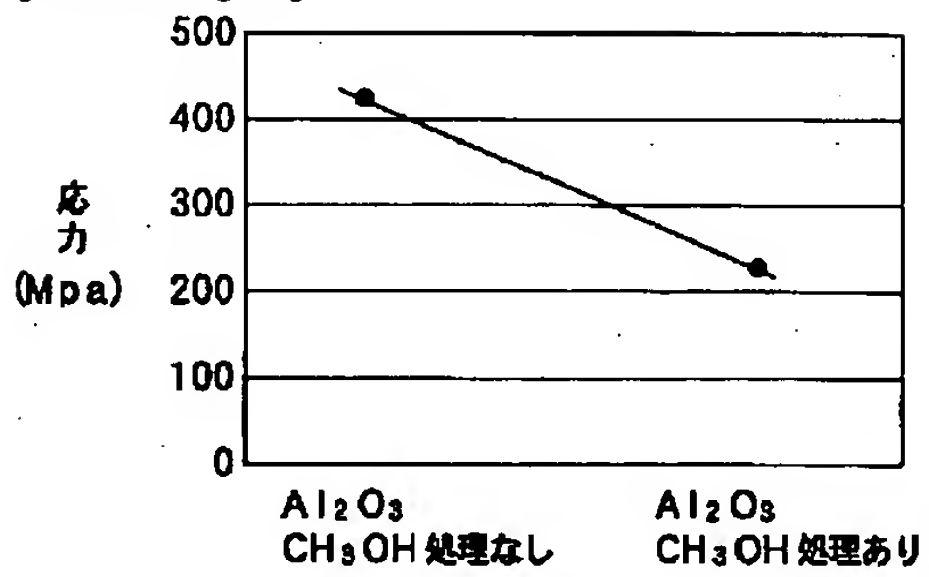
[Drawing 1]



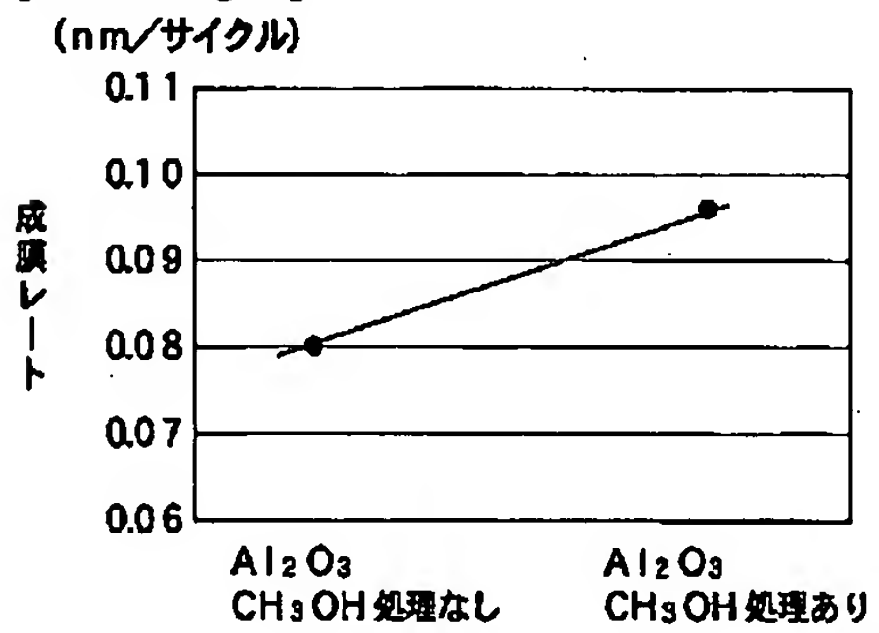
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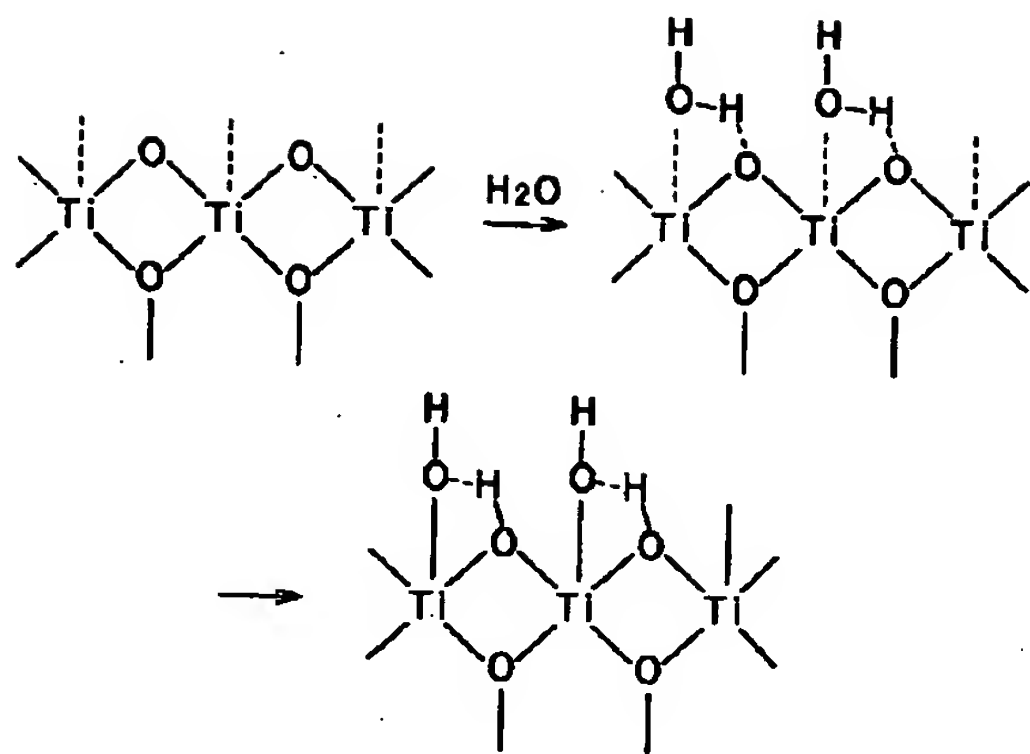
[Drawing 3]



[Drawing 4]



[Drawing 5]



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